

Variation of a Triangular Pattern Shape due to Shrinkage in the Repeated UV Imprint Process

Jiyun Jeong^{*}, Su Hyun Choi^{**}, Young Tae Cho^{**,#}

^{*}HYUNDAI WIA Corp., ^{**}Department of Mechanical Engineering, Changwon National Univ.

반복적인 UV 임프린트 공정에서 수축에 따른 삼각 단면을 가진 패턴의 형상 변화

정지윤^{*}, 최수현^{**}, 조영태^{**,#}

^{*}현대위아(주), ^{**}창원대학교 기계공학과

(Received 24 February 2020; received in revised form 14 April 2020; accepted 16 April 2020)

ABSTRACT

Shrinkage is inevitable in the curing of resins during the nanoimprint process. The degree of shrinkage that occurs as the resin transforms from a viscous liquid to solid differs depending on the type of resin. However, if the cured material is repeatedly cured using the same material, constant shrinkage can be confirmed. In this study, the pattern of change was observed by repeatedly performing the nanoimprint process using a resin with a constant shrinkage rate. The observed pattern for the change of shape was made using a triangular pyramid-shaped aluminum master mold and a flexible replica mold made from the master. Shrinkage that results from the nanoimprint process occurs linearly in the longitudinal direction of the pattern and can be predicted by simple calculations. The change of the pattern due to shrinkage occurred as expected. If the shrinkage rate remains constant, various patterns can be manufactured with high accuracy by correcting these changes before producing a specific shape. This study confirms that the pattern of the desired angle can be obtained by performing the repeated imprint without having to manufacture a master mold.

Keywords : Nanoimprint(나노임프린트), Shrinkage(수축), Viscosity(점성), Repeated Imprint(반복 임프린트)

1. Introduction

Nanoimprint technology was first proposed by Professor S. Y. Chou of Princeton University in 1995^[1,2] and is now emerging as a next-generation lithography technology capable of producing ultra-fine

patterns. In particular, in industries that require high technology, such as biotechnology, new energy such as semiconductors, displays, and solar cells, complex research is not required, and many studies are being conducted because high efficiency can be obtained at low cost. Nanoimprint technology produces a stamp engraved with a desired pattern and presses the resin of a polymer component deposited on a substrate to form a pattern. In this state, ultraviolet

Corresponding Author : ytcho@changwon.ac.kr

Tel: +82-55-213-3608, Fax: +82-55-213-2859

(UV) or thermal energy can cure the resin. If the mold is removed afterward, it can be manufactured from a few nanometers to several tens of nano-fine patterns of a desired shape^[3-20].

In general, the change from a liquid to a solid state results naturally in volume shrinkage. Resin is also a viscous liquid with a polymer component that, when subjected to UV or heat, hardens to a solid state, causing shrinkage. The degree of shrinkage depends on the type of resin, which is considered to be one of the inevitable defects in the imprint process. In this study, we seek to take advantage of the shrinkage, though it is a defect that occurs in the UV imprint process. In particular, we do so by repeatedly performing the imprint process to shrink the pattern to examine how it changes. If the change in the pattern due to shrinkage can be predicted, it can be used as a method for fabricating the pattern.

2. Experiments

Fig. 1 shows a schematic of the UV imprint process using rollers. The resin used in the imprint process is a viscous liquid, which typically consists of monomers, oligomers, and polymers. The covalent bond of the curing step causes shrinkage and reduction of the pattern size. In general, resins used for imprints are known to have shrinkage ratios of less than 1% to as high as 7%, depending on the type. UV curable resins usually have shrinkage rates of approximately 3% to 5%. Therefore, all the models presented in this study were experimented with on the assumption that they had a contraction rate of approximately 4%, which was verified by the experiment. During the imprint process, UV is irradiated in the state in which a mold with a desired shape engraved in it is pressed on a resin applied to a substrate. The resin hardens in response to the UV and inevitably shrinks. Fig. 2 shows the triangular pattern in the form of a line and space

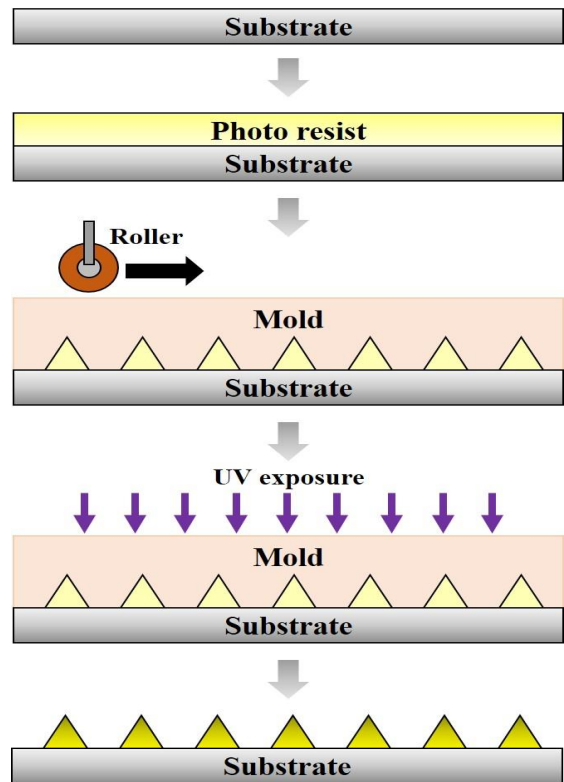


Fig. 1 Schematic diagram of UV imprint process

after the imprint process.

In the imprint process, various variables, including environmental variables, such as temperature and cleanliness, and process variables, such as UV dose, pressurization method, and unfilled phenomena, should be considered in order to obtain the pattern of the desired shape. However, the purpose of this experiment was to observe the change of the pattern shape due to the shrinkage caused by the repeated imprint process. Therefore, the variables affecting the pattern change were limited to the shrinkage. In this case, using the x, y, and z coordinates shown in Fig. 2, it was expected that the shrinkage in the x and z directions of the triangle pattern would be much greater than the shrinkage in the y direction, which is the longitudinal direction of the pattern. Therefore, in this study, it is assumed that there is

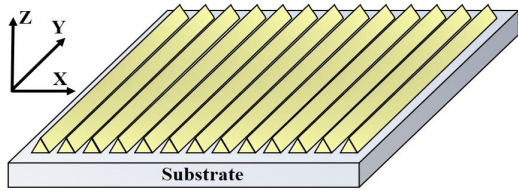


Fig. 2 Model of triangle pattern by imprint process

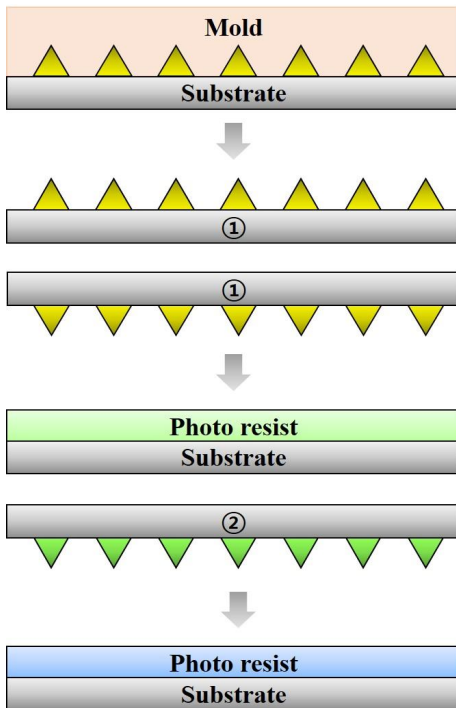


Fig. 3 Repeated imprinting process

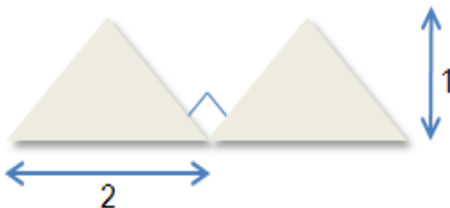


Fig. 4 Suggestion model (Triangle pattern)

no shrinkage in the longitudinal direction; the shrinkage in the cross section (the x and z directions) of the pattern is considered.

3. Theoretical Approach

If the imprint process is performed repeatedly, the shape of the pattern will continue to shrink. Repeatedly performing an imprint implies using a stamp mold that was first produced, as shown in Fig. 3; the pattern is formed by using ① again as a stamp to complete ② and using it again as a stamp.

Continued shrinkage will increase the angle between each pattern and reduce the pattern size in comparison to the original stamp. It is assumed that an imprint process is repeatedly performed by making a stamp engraved with a triangle having an angle of 90° between patterns and aspect ratio is 1:2, as shown in Fig. 4. As described above, if the longitudinal direction of the pattern, that is, the cross section, is referred to as the x and y coordinates, the shrinkage in the z direction does not need to be considered because it is very small compared to the shrinkage in the x and y directions. Because the shrinkage in the x direction is also as small as the shrinkage in the z direction, as the pattern is continuous, only the shrinkage in the y direction is considered, and the shrinkage rate is assumed to be uniformly contracted at 4%.

The ① pattern imprinted using the stamp mold contracts uniformly in comparison to the stamp size, making the angle between the patterns 93° and the length of the longitudinal would be 0.95. Using this mold again as a stamp to produce ② patterns, the length of the ② patterns becomes 0.95 in the longitudinal direction (0.95% of ①). Using the Pythagorean theorem, as shown in Fig. 5, length of the largest side is 1.38. At this time, when the size of the two sides and one cabinet (not the included angle) can be known, the following equation (1) is established by sine law.

$$\frac{1.38}{\sin 90} = \frac{0.96}{\sin \vartheta} \quad (1)$$

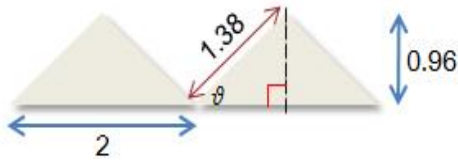


Fig. 5 Expect model by second imprinting

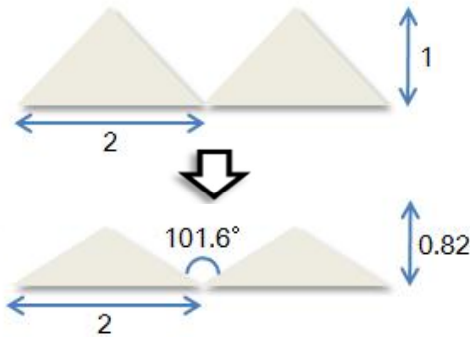


Fig. 6 Variation of pattern shape by fifth imprinting process

Summarizing this equation, it becomes equation (2) and $\theta = 43.5^\circ$.

$$\sin^{-1} \vartheta = \frac{0.96}{1.38}, \quad \vartheta = \sin \frac{0.96}{1.38} \quad (2)$$

At this time, the outer angle of θ is 136.5° , and the angle between the patterns becomes 93° by subtracting 43.5° of the inner angle of the left triangle.

Since the length in the longitudinal direction decreases linearly by contraction, when calculated using the sine law, the pattern of the fifth imprinted triangle is approximately 0.82 in height and 101.6° in the angle between the pattern, as shown in Fig. 6.

4. Experimental Results

The variation of the triangular pattern calculated in the previous section was confirmed through experiments. In the experiments, an aluminum-based

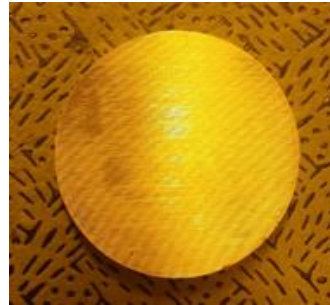


Fig. 7 Aluminum stamp of triangle pattern

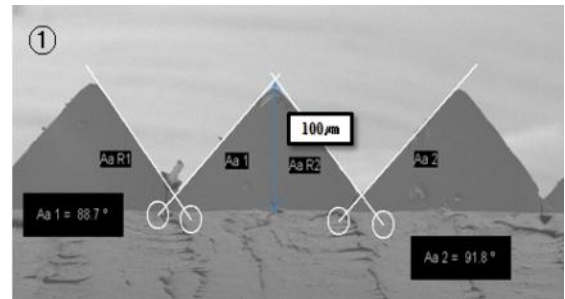


Fig. 8 Cross section image of first imprinting sample

stamp was manufactured, and the UV imprint process was repeated by applying UV curable resin to the PET(Polyethyleneterephthalate) substrate, molding the stamp, and then rolling it. Fig. 7 shows how the stamp was produced. The pattern engraved on the aluminum stamp is triangular with a width of $200\mu\text{m}$ and a length of $100\mu\text{m}$, like the model proposed in the previous section.

In the first imprint process, UV curable resin with a shrinkage rate of 5% or less was applied to the PET and imprinted using a stamp, and UV irradiation was performed with UV power of 1kW for five minutes, according to the curing conditions of resin. After that, the triangle pattern was completed following the demolding process. Fig. 8 shows a cross-sectional view of the pattern completed in the first imprinting process. The cross section of the pattern was photographed using FE-SEM, an electron microscope.

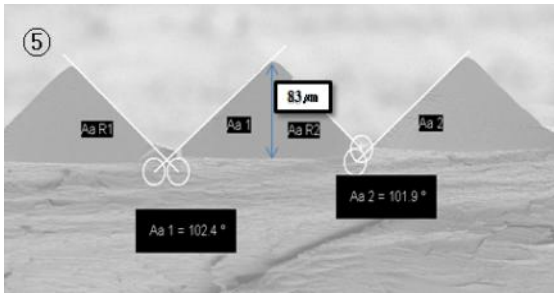


Fig. 9 Cross section image of fifth imprinting sample

The measurements indicate that the angle between the patterns is 91° , and the length in the longitudinal direction of the triangular pattern is similar to that of the relatively produced stamp. (The stamp was manufactured using an aluminum manufacturing process, so mechanical errors may occur.)

The result of repeating the imprint process using the ① pattern as a stamp is shown in Fig. 9. Between each imprint process was carried out to improve the releasability by increasing the curing degree of the resin through post-curing treatment.

As described in Fig. 3, after repeated imprinting using the completed pattern as a stamp, the cross section of the pattern formed after the fifth imprinting process is as shown in Fig. 9. When the imprinting process was repeated five times, the angle between the triangular pattern was approximately 102° and the height was $83\mu\text{m}$. In the previous section, when the formula for linear shrinkage was used to simulate the imprint process being repeatedly performed five times, the value for the angle between the patterns was approximately 101.6° and $82\mu\text{m}$ for the pattern height.

Fig. 10 is a graph comparing the theoretical value and the experimental value according to the deduced shrinkage using the formula. Comparing the theoretical and experimental values of Fig. 10 shows that the length decreases with a similar trend and the angle increases.

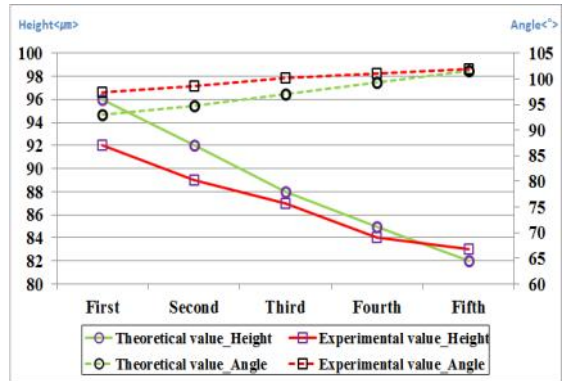


Fig. 10 Comparison of theoretical value with experimental value

5. Conclusion

The shrinkage of the resin that inevitably occurs in the imprint process can be a process defect in transferring the pattern of a desired shape. In this study, however, the resin contracted through reverse conception. Through repeated imprinting, the shape of the pattern changed with the shrinkage of the resin.

The imprint process was repeatedly performed to confirm the variation according to the shrinkage of the triangular pattern with a horizontal and vertical ratio of 1:2 and an angle of 90° . The pattern formed on the fifth imprints had an angle of approximately 102° and a height of $83\mu\text{m}$. It can be seen that the measured experimental value is close to the angle of 101.6° and the height of $82\mu\text{m}$, which are the values derived using the equation outlined in section 3. However, the calculated contraction is linear and shrinks to almost the same value, whereas in the experiment, the shrinkage decreases in relation to the number of times the imprint process is repeated. Increasing the number of repeated imprints is expected to introduce errors into the equation. The shrinkage of the resin in the actual imprint process is non-linear and requires considerations of various factors, such as the degree

of adhesion between the resin and the substrate and the shape of pattern, the residual layer thickness. However, when the number of repeated imprints is small, a contraction close to linear contraction occurs, which is almost equivalent to the calculated amount. When the imprint process is repeated numerous times, the values to be considered increase exponentially, and a more precise calculation formula may be required.

Applicable to various shapes in the future, the approach suggested by this paper makes it possible to check the variation of the shape according to shrinkage and derive an optimal model. The idea proposed in this paper can be used to produce various patterns of a desired shape with one stamp by using the shrinkage of the resin that inevitably occurs during the imprint process.

Acknowledgments

This paper is based upon work supported by the Ministry of Trade, Industry & Energy (MOTIE), Korea, under the Industrial Technology Innovation Program, No. 20000665, Development of ecofriendly and highly durable surface treatment for super omniphobic substrate on a large area of over 4m², Korea Institute for Advancement of Technology (KIAT) (N0002310). The experiment was conducted using the UV imprint equipment of the Smart Manufacturing Technology Center.

References

1. Chou, S. Y., Kroauss, P. R. and Renstrom, P. J., "Imprint of Sub 25 nm Vias and Trenches in Polymers," *Applied Physics Letters*, Vol. 67, No. 21, pp. 3114-3116, 1995.
2. Tan, H., Gilbertson, A., and Chou, S. Y., "Roller Nanoimprint Lithography," *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structure Processing, Measurement, and Phenomena*, Vol. 16, No. 6, pp. 3926-3928, 1998.
3. Ajay, P., Cherala, A., Yin, B. A., Moon, E. E., Fabian Pease, R., and Sreenivasan, S. V., "Multifield Sub-5 nm Overlay in Imprint Lithography," *Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena*, Vol. 34, No. 6, 061605, 2016.
4. Kuwae, H., Okada, A., Shoji, S. and Mizuno, J., "Sub-50-nm Structure Patterning by Combining Nanoimprint Lithography and Anisotropic Wet Etching without Considering Original Mold Resolution," *Microelectronic Engineering*, Vol. 169, pp. 39-42, 2017.
5. Hwang, B., Shin, S. H., Hwang, S. H., Jung, J. Y., Choi, J. H., Ju, B. K. and Jeong, J. H., "Flexible Plasmonic Color Fillters Fabricated Via Nanotransfer Printing with Nanoimprint-based Planarization," *ACS Applied Materials & Interfaces*, Vol. 9, No. 33, pp.27351-27356, 2017.
6. Dallorto, S., Staaks, D., Schwartzberg, A., Yang, X., Lee, K. Y., Rangelow, I. W., Cabrini, S. and Olynick, D. L., "Atomic Layer Deposition for Spacer defined Double Patterning of Sub-10 nm Titanium Dioxide Features," *Nanotechnology*, Vol. 29, No. 40, 405302, 2018.
7. Li, Y., Choi, J., Sun, Z., Russell, T. P., and Carter, K. R., "Fabrication of Sub-20 nm Patterns using Dopamine Chemistry in Self-aligned Double Patterning," *Nanoscale*, Vol. 10, No. 44, pp. 20779-20784, 2018.
8. Nickmans, K. and Schenning, A. P., "Directed Self-Assembly of Liquid-Crystalline Molecular Building Blocks for Sub-5 nm Nanopatterning," *Advanced Materials*, Vol. 30, No. 3, 2018.
9. Ito, S., Kasuya, M., Kawasaki, K., Washiya, R., Shimazaki, Y., Miyauchi, A., Kurihara, K. and Nakagawa, M., "Selection of Diacrylate Monomers for Sub-15 nm Ultraviolet Nanoimprinting by

- Resonance Shear Measurement,” *Langmuir*, Vol. 34, No. 32, pp. 9366-9375, 2018.
10. Pandey, A., Tzadka, S., Yehuda, D. and Schwartzman, M., “Soft Thermal Nanoimprint with a 10 nm Feature Size,” *Soft Matter*, Vol. 15, No. 13, pp. 2897-2904, 2019.
 11. Fan, Y., Zhang, R., Liu, Z., Huang, D. and Chu, J., “Direct Metallic Nanostructures Transfer by Flexible Contact UV-curable Nano-imprint Lithography,” *Applied Physics Express*, Vol. 12, No. 9, 2019.
 12. Woo, J. Y., Jo, S., Oh, J. H., Kim, J. T., and Han, C. S., “Facile and Precise Fabrication of 10-nm Nanostructures on Soft and Hard Substrates,” *Applied Surface Science*, Vol. 484, pp. 317-325, 2019.
 13. Choi, J., Lee, C. C. and Park, S., “Scalable Fabrication of Sub-10 nm Polymer Nanopores for DNA Analysis,” *Microsystems & Nanoengineering*, Vol. 5, No. 1, pp. 1-10, 2019.
 14. Baek, S., Kim, K., Sung, Y., Jung, P., Ju, S., Kim, W., Kim, S. J., Hong, S. H. and Lee, H., “Solution-processable Multi-color Printing using UV Nanoimprint Lithography,” *Nanotechnology*, Vol. 31, No. 12, 2020.
 15. Kwon, S., Kim, Y. J., Lim, H., Kim, J., Choi, K. B., Lee, J. and Kim, G., “Fabrication of a Metal Roller Mold with Nanoimprinted Pattern using Thermal Nanoimprint Lithography,” *Science of Advanced Materials*, Vol. 12, No. 4, pp. 481-485, 2020.
 16. Cho, Y. T. and Jung, Y. G., “Technology for Efficiency Enhancement of Crystalline Si Solar Cell using Nano Imprint Process,” *Journal of the Korean Society of Manufacturing Process Engineers*, Vol. 12, No. 5, pp. 30-35, 2013.
 17. Lee, J., Lee, J., Nam, S., Cho, S., Jo, Y., Go, M., Lee, S., Oh, D. K., Kim, J. D., Lee, J. H. and Ok, J. G., “Development of a Compact Desktop-sized Roll-to-roll Nanoimprinting System for Continuous Nanopatterning,” *Journal of the Korean Society of Manufacturing Process Engineers*, Vol. 16, No. 1, pp. 96-101, 2017.
 18. Jo, J., Kim, W., Kim, K. Y. and Choi, Y. M., “Focused-Infrared-Light Assisted Roll-to-Roll Hot Embossing,” *Journal of the Korean Society for Precision Engineering*, Vol. 34, No. 3, pp. 199-203, 2017.
 19. Choi, H. M., Kwon, S., Jung, Y. G. and Cho, Y. T., “Comparison of Durability for PUA Type Resin using Wear and Nano-indentation Test,” *Journal of the Korean Society of Manufacturing Process Engineers*, Vol. 17, No. 5, pp. 8-15, 2018.
 20. Kwak, M. K., “A Review: Productivity Enhancements of Micro/Nano Patterning Methods,” *Journal of the Korean Society for Precision Engineering*, Vol. 35, No. 11, pp. 1019-1026, 2018.